

REACTION KINETIC MODEL OF THE SURFACE-MEDIATED FORMATION OF PCDD/F FROM PYROLYSIS OF 2-CHLOROPHENOL ON A CuO/Silica SURFACE.

Slawo Lomnicki¹, Lavrent Khachatryan¹, Barry Dellinger¹

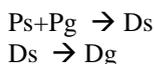
¹Louisiana State University, Department of Chemistry, Baton Rouge, USA

Introduction

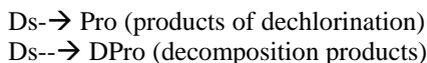
One of the major challenges in developing predictive models of the surface mediated pollutant formation and fuel combustion is the construction of reliable reaction kinetic mechanisms and models. While the homogeneous, gas-phase chemistry of various light fuels such as hydrogen and methane is relatively well-known^{1,2}, large uncertainties exist in the reaction paths of surface mediated reaction mechanisms for even these very simple species.

To date, no detailed kinetic consideration of the surface mechanisms of formation of complex organics such as PCDD/F have been developed. In addition to the complexity of the mechanism, a major difficulty is the lack of reaction kinetic parameters (pre-exponential factor and activation energy) of surface reactions. Consequently, numerical studies of the surface-mediated formation of PCDD/F have often been incorporated only a few reactions.

In 1983 the first attempt to model catalytic formation of PCDD/F was performed by Shaub and Tsang³. They proposed a two-step heterogeneous mechanism to explain the levels of dioxins observed in flue gases:



where P is precursor, D is dioxin, s is surface and g is gas phase. This mechanism resembles the so-called Eley-Rideal (ER) mechanism widely discussed in literature together with the Langmuir-Hinshelwood (LH) mechanism^{4,6}. A significant adjustment to the kinetic parameters of this mechanism and an extended, four step global scheme was subsequently proposed⁴. These new steps were:



More recently a modified catalytic model to explain PCDD formation on fly-ash surfaces was suggested⁵. This four-step global model was based on the assumption that coupling of two

chlorophenol molecules adsorbed on a fly-ash surface forms PCDD through a Langmuir-Hinshelwood (LH) type mechanism.

We report the development of a numerical multiple-step surface model based on experimental data of surface mediated (5% CuO/SiO₂) conversion of 2-monochlorophenol (2-MCP) to PCDD/F under pyrolytic ⁷ or oxidative ⁸ conditions. A reaction kinetic model of the catalytic conversion of 2-MCP on the copper oxide catalyst under pyrolytic conditions was developed based on a detailed multistep surface reaction mechanism developed in our laboratory^{7, 8}. The performance of the chemical model is assessed by comparing the numerical predictions with experimental measurements. SURFACE CHEMKIN (version 3.7.1) software was used ⁹ for modeling.

Our results confirm the validity of previously published mechanism of the reaction and provides new insight concerning the formation of PCDD/F formation in combustion processes. This model successfully explains the high yields of PCDD/F at low temperatures that cannot be explained using a purely gas-phase model ^{10, 11}.

Model Development

Four assumptions were made in the development of our reaction kinetic model;

1. The order of magnitude of kinetic parameters (especially pre-exponential factors) is based on typical values from surface transition-state theory ¹²⁻¹⁴.
2. Modifications of the pre-exponential factors and the activation energies have been compared for analogous systems and fitted with the experiment by other investigators ³⁻⁵.
3. Gas-phase reaction kinetic parameters could be adapted to surface conditions. Activation energy for the gas phase reaction was considered as upper limit for the same surface reaction. Decreasing the activation energy of the corresponding surface reaction was a common approach ^{15, 16}.

4. Kinetic parameters estimated based on the assumptions 1-3 were fitted to the experimental rates of formation of PCDD and PCDF in our experiments.

Table 1: Core model for the Surface catalyzed formation of PCDD/F

SURFACE REACTIONS CONSIDERED *	(k = A T ⁿ exp(-E/RT))			Units
	A	n	E	
1. C6H4OHCL+OH(S) => C6H4OCL(S)+H2O	2.00E+12	0.0	21000.0	cm3/mol.sec
2. C6H4OCL(S)+H2O=>C6H4OHCL+OH(S)	1.00E+13	0.0	25000.0	cm3/mol.sec
3. C6H4OCL(S) => C6H4OCL(S,en)	1.00E+12	0.0	0.0	s-1 e-transfer
4. C6H4OCL(S,en)=>C6H4OCL(S,ke)	1.00E+12	0.0	0.0	s-1
5. C6H4OCL(S,ke) => C6H4OCL(S,en)	5.00E+12	0.0	0`0	s-1
FURAN FORMATION, LH MECHANISM				
6. 2C6H4OCL(S,ke)=>C12H8O2CL2(S)`	1.00E+21	0.0	21000.0	cm2/mol.sec
7. C12H8O2CL2(S)=>C12H6OCL2+H2O	1.00E+12	0.0	33500.0	s-1
PRECURSOR FOR DIOXIN FORMATION				
8. C6H4OCL(S,ke)+O(S)=>C6H4O2CL(S,oe)	6.00E+22	0.0	0.0	cm2/mol.sec
9. C6H4O2CL(S,oe)=>C6H3CLOOH(S)	2.00E+13	0.0	18000.0	s-1
DIOXIN FORMATION, ER MECHANISM				
10. C6H3CLOOH(S)+C6H4OHCL =>C12H8O3CL(S)+HCL	6.0E+17	0.0	20000.0	cm3/mol.sec
11. C12H8O3CL(S)=>C12H7O3(S)+HCL	1.00E+13	0.0	20000.0	s-1
12. C12H7O3(S) => O(S)+8C+0.5CO+0.5CO2+1.5C2H4+0.5H2O	5.00E+12	0.0	37000.0	s-1
13. C12H7O3(S)+H2O =>C12H8O2+O(S)+OH(S)	6.00E+17	0.0	7000.0	cm3/mol.sec
DIOXIN FORMATION, LH MECHANISM				
14. C6H4OCL(S,en)+C6H4OCL(S,en) => C12H8O2CL(S)+CL	1.00E+21	0.0	23000.0	cm2/mol.sec
15. C12H8O2CL(S)=>C12H8O2+CL	6.00E+13	0.0	12000.0	s-1
16. C6H4OCL(S)=>C2H2+CO+3C+HCL+0.5H2	5.00E+12	0.0	37000.0	s-1

* (S) - surface species; (S,ke), (S,en) - keto-enol forms of mesomers; (S,oe) - keto form bounded to surface oxygen; O(S) - the terminal oxygen ion on CuO.

Using this framework, a 16 step surface model was developed by optimizing the kinetic parameters in the reaction mechanism previously developed in our laboratory ^{7, 8}. The detailed mechanism and reaction parameters are depicted in Table 1. Each reaction expression is in the SURFACE CHEMKIN format (PLUG Application). The Surface CHEMKIN has broad capabilities to solve complex chemical and physical problem ⁹.

The input conditions for the PLUG input file were the same as the same as our previously reported experimental reaction conditions ⁷: 2-chlorophenol concentrations – 88 ppmv in a helium atmosphere, flow rate 1.0 to 1.5 cm³/min (to maintain a constant contact time with the catalyst bed of ~ 0.2 sec over a temperature range of 473 - 723 K.

The outputs of the model were the final concentrations of all species included in the reaction mechanism (Table 1). It is worth mentioning that in SURFACE CHEMKIN, a reaction rate has units of mole/(cm²•sec). The rate constants of ER type of reactions have units of cm³/(mole•sec),

and LH type reactions have units of $\text{cm}^2/(\text{mole}\cdot\text{sec})$. For a reaction involving only one surface-species CHEMKIN assumes units of sec^{-1} .

A very low surface coverage between 0.001 - 0.0001 (typical for incinerator measurements¹⁷) was used. Although estimation of the surface coverage of potential precursors involved considerable uncertainty, we believe that for our experimental conditions^{7, 8} (5% CuO/SiO₂, 500 m²/g) low coverage is achieved. For comparison the surface area of a fly-ash is only ~ 1-10m²/g⁶.

Discussion

This reaction kinetic model is based on the reaction mechanism developed according to the experimental kinetic and quantitative data for 2-Monochlorophenol conversion over CuO/Silica catalyst⁷. It is the only detailed mechanism describing the surface catalyzed formation of PCDD/F. The mechanism consists of five groups of reactions:

1. Adsorption of reactant 2-MCP.
2. Surface reactions of adsorbed 2-MCP and reaction intermediates.
3. Desorption of principal degradation products CO, HCL, H₂, H₂O etc.
4. Formation of major PCDD/F products from the reaction of 2-MCP, dibenzo-p-dioxin (DD) and 4,6-dichlorodibenzofuran (DCDF).
5. Desorption of DD and DCDF.

The Surface CHEMKIN modeling calculations based on this mechanism have shown that the maximal calculated yields of DCDF and DD were higher than experimental measurements by factor of ~2-2.5 in the temperature range from 550 to 700 K.

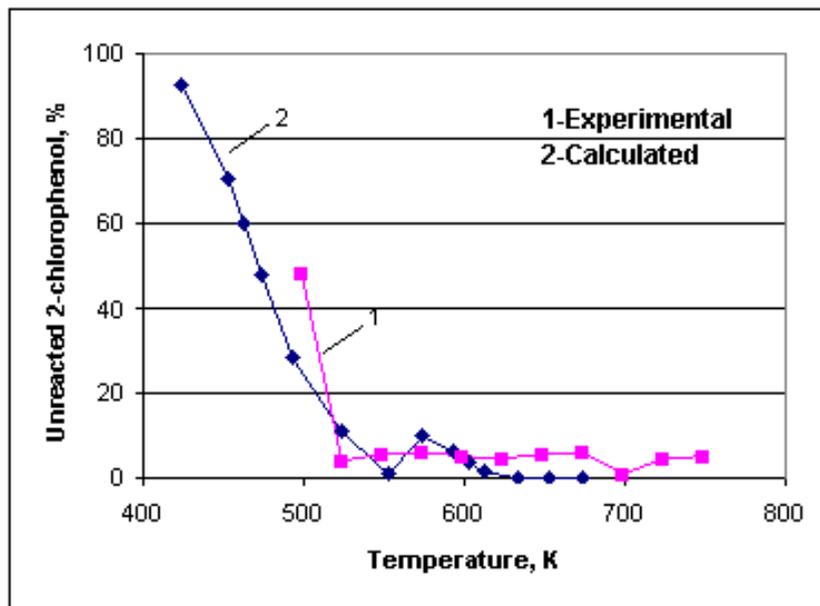


Fig.1. Experimental (1) and calculated (2) curves for total 2-MCP conversion.

It is interesting to compare two ER and LH mechanisms for formation of DD and DCDF. While for DCDF formation there is a single LH mechanism in the scheme, rxns 6,7, the formation of DD can be explained by two-ER and LH mechanisms (Table 1). Modeling calculations have shown that removing reactions 14 and 15 (LH mechanism for DD formation) from the scheme do not significantly effect the DD yields (decreasing only ~ 5%). DCDF yields also remain nearly unchanged (no influence on consumption of 2-chlorophenol). In contrast removal of reactions 10-13, for the ER mechanism for DD formation, result in a decrease in DD yield by factor of more than 3 at unchanged yields of DCDF. The same affect is observed for the dependence of DD yields on initial 2-MCP concentration. DD concentrations decrease by a factor of 1.3 at 523 or 573K by decreasing the initial 2-MCP concentration by a factor of 1.5.

We did not observe any significant dependence on the initial concentration at higher temperatures (>633 K), since chlorophenol is decomposed completely (Fig. 1) under these conditions. We observe good correlation between experimental (curve 1) and calculated unreacted 2-MCP (curve 2) concentration versus temperature.

An arrhenius expression for the consumption of 2-MCP versus reaction temperature yields an activation energy for catalytic conversion of 2-MCP over 5% CuO/SiO₂ of ~ 15 kcal/mol (Fig.2). This value is in good agreement with the activation energies for a catalytic conversion processes for a series of analogous compounds, i.e. hydroquinone with $E_a \sim 10$ kcal/mol and catechol with $E_a \sim 16$ kcal/mol on iron oxide nano-particles¹⁸.

Thus we have made a first attempt at development of an expanded reaction kinetic model including 16 surface reactions to explain the yields of DD and DCDF from chlorinated phenols using 2-MCP and 5% CuO/silica as a model fly-ash surface. The calculated yields of DCDF and DD correlated well with experimental observations⁷.

The principal difference is that due to the steric hindrance of oxygen centered radical on the surface, the radical-radical reactions for DD formation are not favorable (although the same reactions are dominant in the gas phase). Radical (surface bounded) – molecule (gas

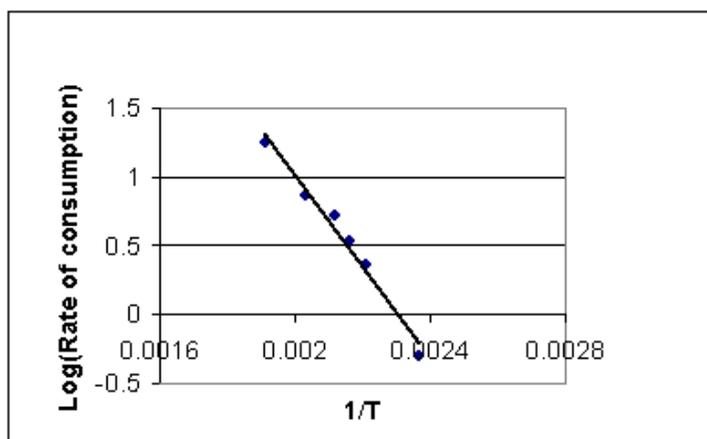


Fig.2 Arrhenius dependence of total maximal rate of conversion of 2-MCP as a function of $1/T$.

phase) reaction is the preferable for DD formation. These results suggest that an Eley-Rideal mechanism involving a gas-phase molecule and surface-bound radical is responsible for DD/DCDF formation on surfaces.

References

- 1 J. A. Miller, Bowman, C.T., *Prog. Energy Combust. Sci.*, 1989, **15**, 287.
- 2 M. Frenklach, Wang, H., Goldenberg, M., Smith, G.P., Golden, D.M., Bowman, C.T., Hanson, R.K., Gardiner, W.C., Lissianski, V., *GRI-Mech. - An optimized detailed reaction mechanism for methane combustion*, *Gas Research Institute*, 1995.
- 3 W. M. Shaub and W. Tsang, in 'Overview of dioxin formation in gas phases under municipal incinerator conditions', 1985.
- 4 E. R. Altwicker, J. S. Schonberg, N. V. Konduri, and M. S. Milligan, Polychlorinated Dioxin/Furan Formation in Incinerators, *Hazardous Waste and Hazardous Materials*, 1990, **7**, 73.
- 5 H. Huang and A. Buekens, Chemical kinetic modelling of PCDD formation from chlorophenol catalysed by incinerator fly ash, *Chemosphere*, 2000, **41**, 943.
- 6 M. S. Milligan and E. Altwicker, Chlorophenol reactions on fly ash. 2. equilibrium surface coverage and global kinetics, *Environmental Science and Technology*, 1996b, **30**, 230.
- 7 S. Lomnicki and B. Dellinger, Formation of PCDD/F from the Pyrolysis of 2-

- ChloroPhenol on the Surface of Disperced Copper Oxide Particles,*Proceedings of the International Symposium on Combustion*, 2003, **29**, 2463.
- 8 S. Lomnicki and B. Dellinger, A Detailed Mechanism of The Surface-Mediated Formation of PCDD/F from the Oxidation of 2-Chlorophenol on CuO/ Silica Surface,*Journal of Physical Chemistry A*, 2003, **107**, 4387.
 - 9 R. J. Kee, Rupley, F.M., Miller, J.A., Coltrin, M.E., Grcar, J.F., Meeks, E., Moffat, H.K., Lutz, A.E., Dixon-Lewis, G., Smooke, M.D., Warnatz, J., Evans, G.H., Larson, R.S., Mitchell, R.E., Petzold, L.R., Reynolds, W.C., Caracotsios, M., Stewart, W.E., Glaborg, P., Wang, C., Adigun, O., Houf, W.G., Chou, C.P., and Miller, S.F., Chemkin Collection, Release 3.7, Reaction Design, Inc., *San Diego, CA*, 2002.
 - 10 L. A. Khachatryan, Burcat, A., and Dellinger, B., An Elementary Reaction Kinetic Model for the Gas-Phase Formation of 1,3,6,8- and 1,3,7,9-Tetrachlorinated Dibenzo-p-dioxins from 2,4,6-Trichlorophenol, *Combustion and Flame*, 2003, **132**, 406.
 - 11 A. R. Khachatryan L., Dellinger B., Development of an expanded and core kinetic model for the gas phase formation of dioxins from chlorinated phenols., *Chemosphere*, 2003, **52**, 695.
 - 12 O. V. Krylov, Kislyuk, M.U., Shub, B.R., Gezalov, A.A., Maksimova, N.D., and Rufov, Yu.N., The rate constants of elementary heterogeneous catalytic reactions, *Kineyika i katakiz*, 1972, **13**, 598.
 - 13 M. Boudart, and Djega-Mariadassou, G., Kinetics of Heterogeneous Catalytic Reactions., *Princeton University Press, Princeton, NJ*, 1984.
 - 14 V. P. Zhdanov, Preexponential Factors for Elementary Surface Processes, *Catal. Rev. - Sci. Eng.*, 1988, **30**, 501.
 - 15 S. M. Walas, *Reaction Kinetics for Chemical Engineers. Butterworth, Boston.*, 1989, 51.
 - 16 B. R. Stanmore, Modeling the formation of PCDD/F in solid waste incinerators, *Chemosphere*, 2002, **47**, 565.
 - 17 E. R. Altwicker, J. S. Schonberg, R. K. N. V. Konduri, and M. S. Milligan, Polychlorinated dioxin/furan formation in incinerators, *Hazard. Waste Hazard. Mater.*, 1990, **7**, 73.
 - 18 E.-J. Shin, Chan, G., Rasouli, F., and Hajaligol, M.R., Reduction of Catechol and Hydroquinone by Catalyst and Amonia, *5th Philip Morris USA Symposium on Fundamental Science, Richmond, Virginia, October 28-30, , p20.*, 2003.